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**INTERIM REPORT ON
CHEMICAL AND THERMAL ANALYSIS**

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REFERENCES



SYNOPSIS

Thermal decomposition activation energies have been determined using two methods of Thermogravimetric Analysis (TGA), with good correlation being obtained between the two techniques. Initial heating curves indicated a two-component system for Coflon (i.e. polymer plus plasticizer) but a single component system for Tefzel. Two widely differing activation energies were for Coflon supported this view, 15 kcal/mol being associated with plasticizer, and 40 kcal/mol with polymer degradation. With Tefzel, values were 40-45 kcal/mol, the former perhaps being associated with a low molecular weight fraction. Appropriate acceleration factors have been determined.

Thermomechanical Analysis (TMA) has shown considerable dimensional change during temperature cycles. For unaged pipe sections heating to 100°C and then holding the temperature resulted in a stable thickness increase of 2%, whereas the Coflon thickness decreased continuously, reaching -4% in 2.7 weeks. Previously-strained tensile bars of Tefzel expanded on cooling during TMA.

SEM performed on H₂S-aged Coflon samples showed significant changes in both physical and chemical nature. The first may have resulted from explosive decomposition after part of the aging process. Chemically extensive dehydrofluorination was indicated, and sulfur was present as a result of the aging. These observations indicate that chemical attack of PVDF can occur in some circumstances.

1.0 Determination of Activation Energies for Coflon and Tefzel Pipe Materials Using Thermogravimetric Techniques

1.1 Description

Method 1 - Variable Temperature Rate Tests

This thermogravimetric technique involves heating replicate specimens separately at differing temperature ramp rates while monitoring weight loss [1]. Figures 1 and 2 show these weight loss curves for Tefzel and Coflon pipe respectively. From the thermal curves, the time required to reach a certain weight loss value is obtained. The activation energy is then determined using the method of Flynn and Wall [2] by plotting logarithm of heating rate versus the reciprocal of temperature of constant decomposition level,

$$E(a) = \frac{-R}{b} \left[\frac{d \log \beta}{d(1/T)} \right] \quad (1)$$

where:

E(a) = Activation Energy (cal/mol)
R = Gas Constant (1.987 cal/mol)
T = Temperature at Constant Conversion (°K)
β = Heating Rate (°C/min.)
b = Constant (= 0.457)

The value of the derivative term (d log β / [d(1/T)]) is the slope of the line in the Arrhenius plots. The activation energy is then used to determine acceleration factors under conditions of elevated temperature exposure.

Method 2 - Constant Temperature Tests

This is also a thermogravimetric method. In this case the specimen is heated to a predetermined temperature and the amount of time required to achieve a certain level of weight loss is recorded. Several different temperatures are used to construct an Arrhenius plot with log time to a certain percentage weight loss versus the reciprocal of the corresponding temperature. The acceleration factor can then be calculated using the following equation:

$$A = \exp \left[\frac{E(a)}{r} \left(\frac{1}{T_s} - \frac{1}{T_t} \right) \right] \quad (2)$$

Where:

A = Acceleration Factor
E(a) = Activation Energy (kcal/mol)
r = Boltzmann's Constant,
T_s = Service Temperature (°K)
T_t = Test Temperature (°K).

1.2 Results

Figure 2 gives strong evidence for two components for Coflon, because of the transient step. In contrast, Figure 1 indicates a single component situation.

Figures 3-7 show Arrhenius plots obtained from isothermal experiments on Coflon pipe specimens. The time necessary to achieve a certain percentage weight loss is plotted versus the independent variable, temperature.

Figures 8-14 show Arrhenius data plots obtained from tests on Tefzel pipe specimens. In these cases the tests were performed at different heating rates, displayed as log heating rate. The temperature at which a certain level of decomposition is obtained is plotted vs. the heating rate.

Coflon was tested by both techniques, while the Tefzel has only been tested by the variable heating rate technique. Taking the $E(a)$ values from the previous figures, activation energy vs. percent weight loss is displayed in Figure 15. Note that comparison between the variable heating rate experiments and isothermal tests shows a good correlation between the two methods. The activation energy has a relatively low value, ≈ 15 kcal/mol, attributed to plasticizer diffusing out of the polymer. When most of the plasticizer is removed ($\approx 11\%$ by weight for Coflon) the activation energy moves to a higher level, ≈ 40 kcal/mol, now presumably relating to polymer degradation.

Figure 16 shows a similar plot of activation energy vs. percent weight loss for Tefzel pipe material. Here the activation energy begins at 40 kcal/mol during the early weight loss process and stabilizes at 45 kcal/mol at the higher percentage weight losses. The early weight loss may be due to loss of low molecular weight components from the Tefzel.

Figures 17-19 show the acceleration factors associated with the three activation energy values described above. As expected the biggest difference seen when comparing these plots arises from the low acceleration factors associated with the evolution of plasticizer from Coflon. This is a result of the fact that the diffusion process is a relatively rapid process by itself and, therefore, temperature does not accelerate the process appreciably.

The diffusion of plasticizer from Coflon is illustrated in the photo in Fig 20. It shows the surface appearance of the inside diameter of the Coflon before and after aging in a 100°C oven. Note the plasticizer collecting in droplets on the surface of the heat aged specimen.

2.0 Thermomechanical Analysis (TMA)

2.1 Analysis of Yielded Tefzel Specimen

Investigation of the yielded gauge-length portions of the previously methanol exposed Tefzel specimens has been performed. Specimens were cut from the center of yielded tensile bars. After placing the specimen in the test chamber the temperature was lowered to -150°C after which the temperature was ramped to +200°C while monitoring dimensional changes,

Table 1 summarizes the results. These specimens, having been stressed beyond the yield point, contain extreme residual stresses as evidenced by the data in Table 1. All of the yielded specimens tested thus far have expanded in the axial direction during the initial cooling cycle (observed but not plotted). This unusual feature perhaps arises from stresses remaining from the earlier mechanical testing. During the ramp to +200°C shrinkage in the axial direction amounts to about 30% while width and thickness increase by about 25%.

The control (no stress and no methanol exposure) shrinks through the thickness by 13%. This may be due to residual stresses occurring during the extrusion process.

2.2 Analysis of Unaged Tefzel and Coflon Pipe Specimens

TMA was performed on pipe sections of unaged Tefzel and Coflon which had experienced no previous stress. The pipe specimens had the following dimensions.

1. Coflon with 5 mm wall thickness and 70 mm i.d..
3. Tefzel pipe 3 mm wall thickness and 35 mm i.d.

Sections which were cut from the pipe samples were placed in the TMA specimen chamber. The temperature was ramped from ambient to 20°C/ minute up to 100°C where it was held isothermally while monitoring dimensional change in the thickness of the specimen.

Figure 21 shows the results for the tests; note that 100°C is reached after about 4 minutes. During the temperature ramping portion of the test, Tefzel expanded slightly up until reaching 65°C at which point a small amount of shrinkage occurred. This was followed by significant expansion beginning at 95°C. After several minutes at 100°C the specimen seems to have stabilized and is equilibrating.

In contrast to the Tefzel behavior, Coflon begins to shrink immediately during the temperature ramp and continues to shrink throughout the test run. After 27,000 minutes (2.7 weeks), the specimen thickness is still decreasing and it appears that much more time is needed to reach equilibrium.

The dimensional changes occurring in the Tefzel pipe sample have been characterized in all three directions - wall thickness, axial, and circumferential. The equilibrated results are shown in Figure 22.

3.0 Scanning Electron Microscopy (SEM) and X-RAY Analysis of Aged Coflon

Scanning Electron Microscopy was performed on sections cut through aged Coflon samples (5% H₂S 7days 120°C, followed by methane permeation at 2500 psi and 130°C for 1 day). Figures 23-31 provide a visual and chemical mapping through the bulk of the samples. Videotaping of the SEM samples was also performed. The analysis was conducted using a Amray 1820 Scanning Electron Microscope interfaced with a Kevex Multichannel Analyzer for elemental detection and mapping.

The micrographs indicate an extremely smooth surface for the unaged Coflon material. Micrographs at the same magnification indicate a crater filled cavernous surface with the aged Coflon material. The topography extends throughout the thickness of the sample not just on the surface. This is similar to the surfaces observed when PVC is aged and embrittled after long term outside aging. This may well be the result of explosive decompression at the end of the permeation testing.

The x-ray analysis of the aged sample indicates the presence of a high level of sulfur (decreasing from sample surface to center) and smaller amounts of Calcium, Zinc, and Silica. The calcium and zinc could be involved in the stabilizer package for the polymer. The silica is probably from some dust contamination of the surface. No fluorine peak is evident in the aged Coflon sample, it is lost in the baseline. The unaged x-ray analysis indicates a very strong absorption of Fluorine in the spectrum. No other elements are obvious in the spectra of the unaged Coflon. It is well known that sulfur can shield the fluorine peak; however, it is surprising to see such a strong peak totally absent in the aged specimen. A tremendous decrease in the fluorine content on the surface of the aged Coflon also was shown previously by ESCA [3].

4.0 Elemental Analysis of Aged and Unaged Coflon

In order to substantiate the ESCA results described previously, [3] and the x-ray analysis, bulk elemental analysis was performed on the samples described in Section 3.0. Tables 2 and 3 compare the elemental analysis results with the ESCA results. Interestingly, the relative carbon content is apparently increasing in both the interior and on the surface of the material after aging. Also note that the sulfur content within the bulk material after aging compares well with the concentrations found on the surface of the aged material. These facts coupled with the relative increase in hydrogen concentration in the interior of the specimen indicate that the mechanism occurring at both the surface and interior of the aged specimen may be dehydrofluorination followed by partial crosslinking with sulfur. What role the plastizer, or other gases present during aging, play in accelerating the process (if any) is unknown at this point.

REFERENCES

1. R.L. Blaine, "Estimation of Polymer Lifetime by TGA Decomposition Kinetics", DuPont Co. Analytical Instruments Application Brief, (1983).
2. J.H. Flynn, et al, Polymer Letters, B4, 323, (1966)
3. J.W. Bulluck and R.A. Rushing, "CAPP Interim Report on Chemical Analysis", CAPP/T.1, June 1994.

Condition	Time in Methanol min.	Δ Length (%)	Δ Width (%)	Δ Thickness (%)	Δ Volume (%)	α_1 -145 TO 10°C PPM/C	α_2 100 TO 110°C PPM/C	α_3 150 TO 175°C PPM/C
NGL CHS=50	0	-33	26	22	0.47	-8	-3812	-2807
NGL CHS=50	27	-29	21	23	0.70	-5	-2760	-2447
NGL CHS=50	54	-30	25	18	0.36	2	-3643	-2683
NGL CHS=50	10000	-8	4.07	5	0.14	-1	-57	-1727
NS	0	2	1	-13	-1.32	85	628	262

NGL = Necked Gauge Length

NS = Not Stressed

CHS = Crosshead Speed (mm/min)

Table 1 - Dimensional Properties of Yielded Tefzel 280; The delta values (difference) were calculated using the dimension of the specimen at 25°C before and after the test cycle to -150°C, +200°C and back. The coefficients of thermal expansion (α) indicated are for the axial direction only.



Specimen	C	N	H	F	S
5% H ₂ S 7days 130°C, methane permeation at 2500 psi and 130°C	71.5	7.3	11.5		1.29
Coflon Control (unaged)	40.7		4.1		<0.1

Table 2 - Elemental Analysis Results for Coflon Elemental Composition data measured from the bulk interior of specimen.

Specimen	C	N	O	F	Si	S	Fe	Zn
Coflon COF4 Aged in 5% H ₂ S at 140°C 1000 psi for 7 days No Permeation	75	3.1	14	1.6	4.1	1.3	0.5?	0.4
Coflon Control (unaged)	52	---	3.1	44	0.3	0.1?	---	---

Note: ? = weak signal
--- = no signal detected

Table 3 - ESCA Results for Coflon Elemental Composition data measured from the surface (approximately the top 100 Angstroms) of each sample and expressed in atomic percent units for the elements detected.

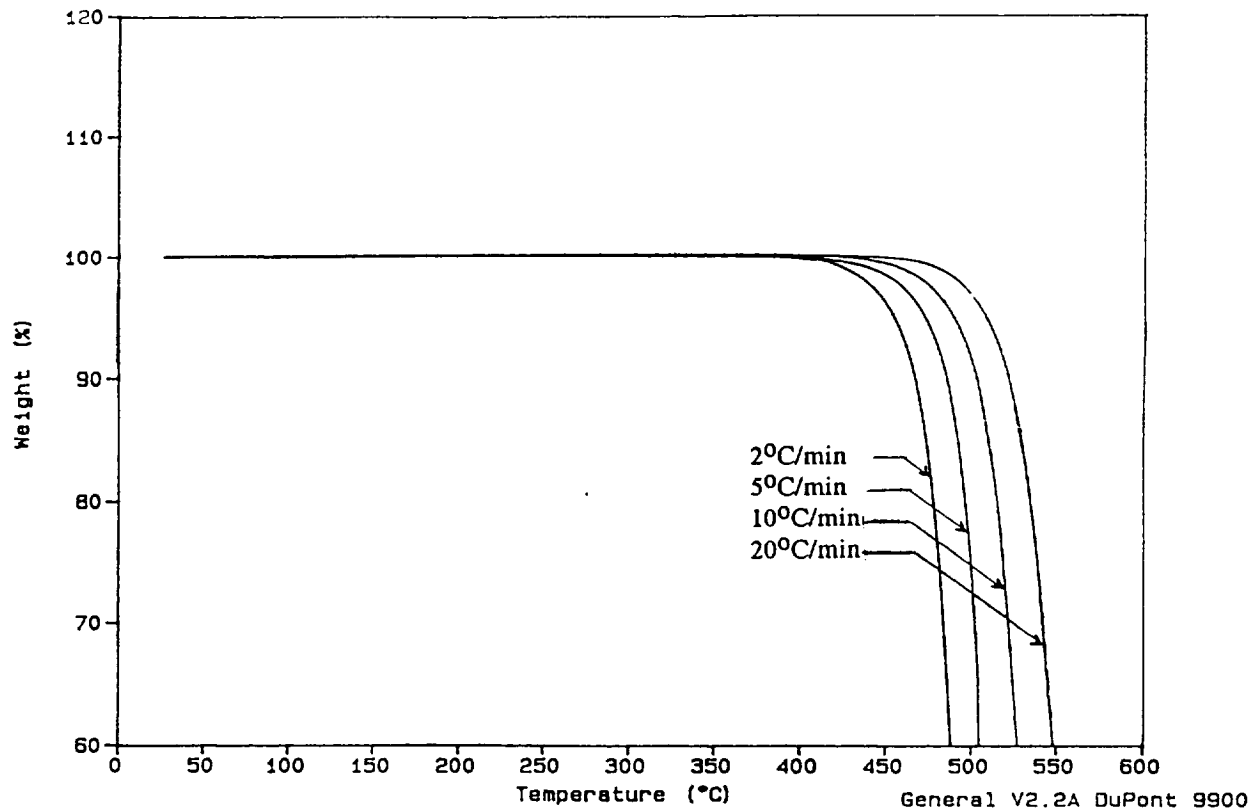


Figure 1 - TGA heating curves for Tefzel at four different ramp rates

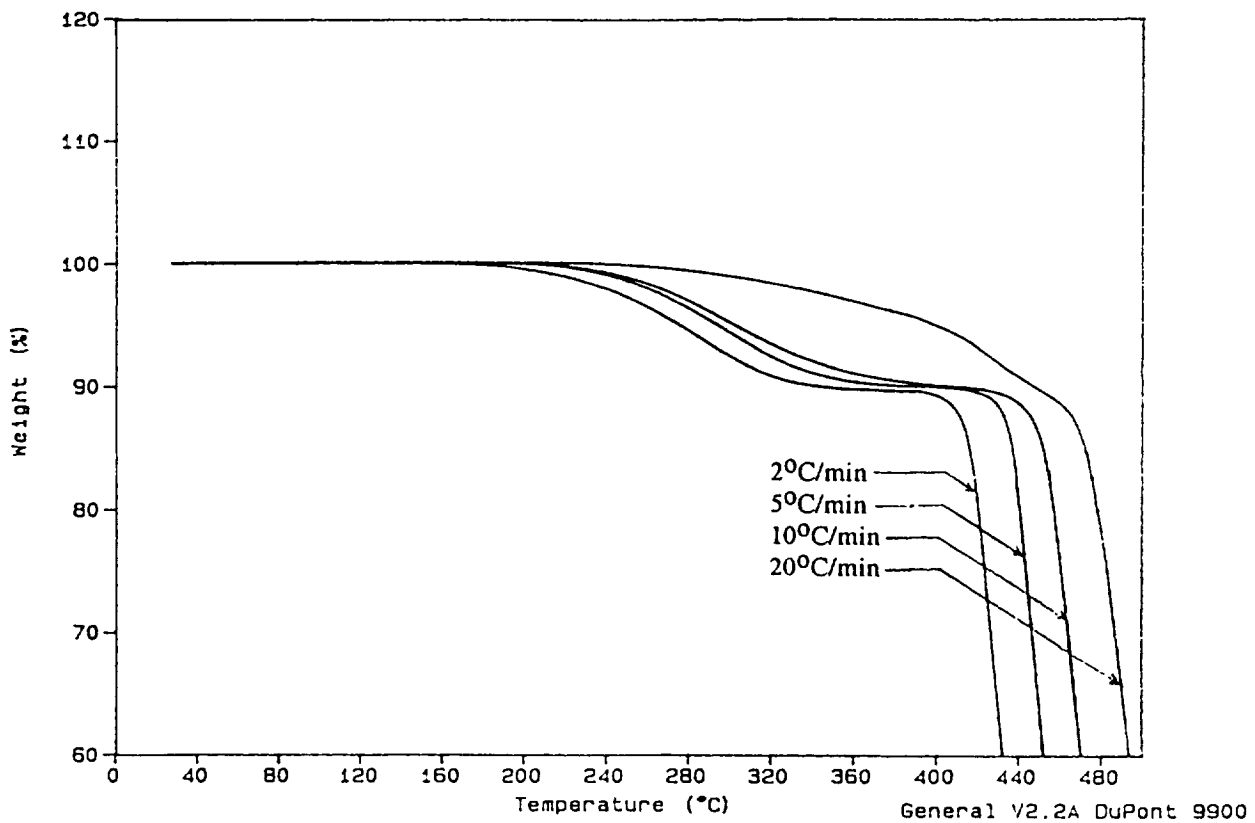


Figure 2 - TGA heating curves for Coflon at four different ramp rates

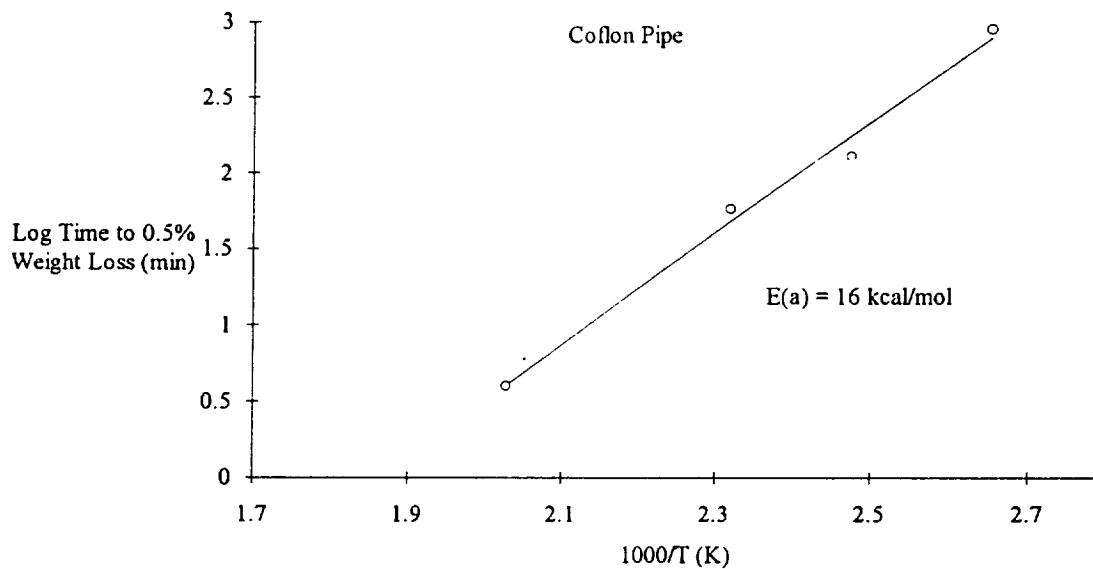


Figure 3 - Arrhenius plot obtained from four separate isothermal experiments; time to 0.5% weight loss; Coflon pipe specimens.

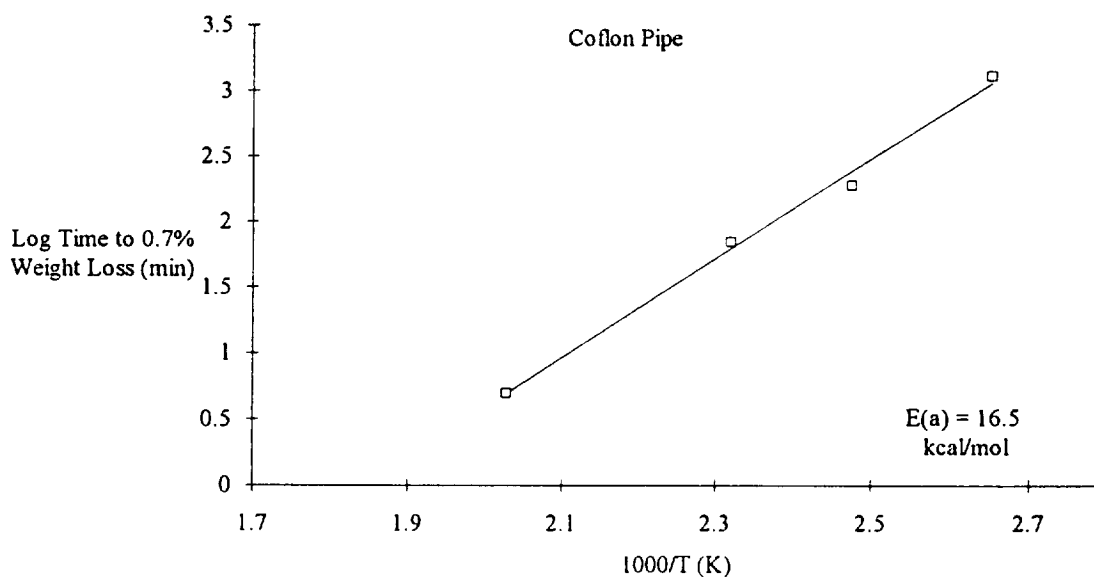


Figure 4 - Arrhenius plot obtained from four separate isothermal experiments; time to 0.7% weight loss; Coflon pipe specimens.

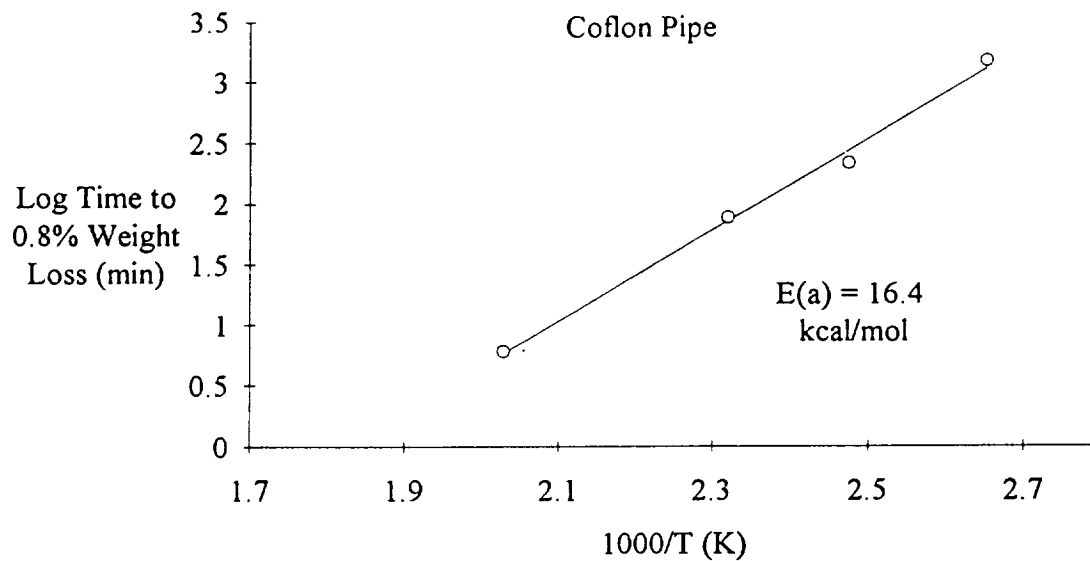


Figure 5 - Arrhenius plot obtained from four separate isothermal experiments; time to 0.8% weight loss; Coflon pipe specimens.

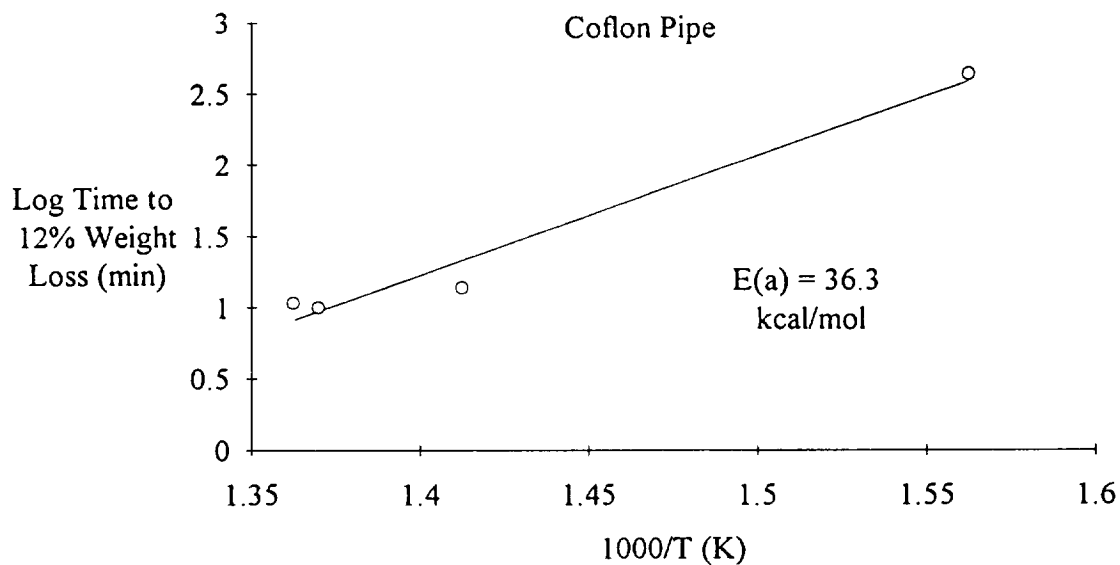


Figure 6 - Arrhenius plot obtained from four separate isothermal experiments; time to 12% weight loss; Coflon pipe specimens.

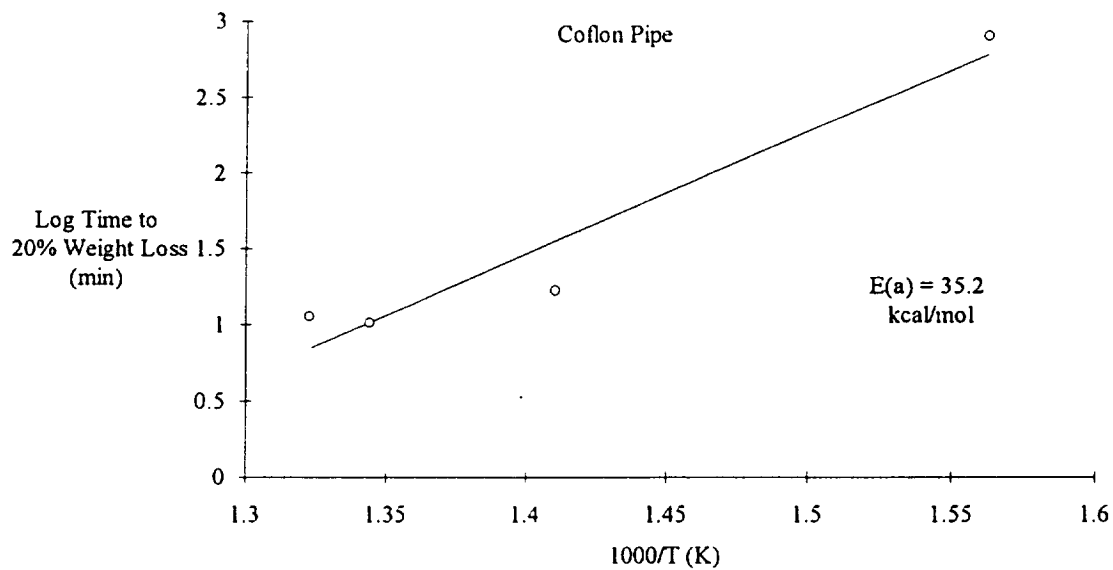


Figure 7 - Arrhenius plot obtained from four separate isothermal experiments; time to 20% weight loss; Coflon pipe specimens.

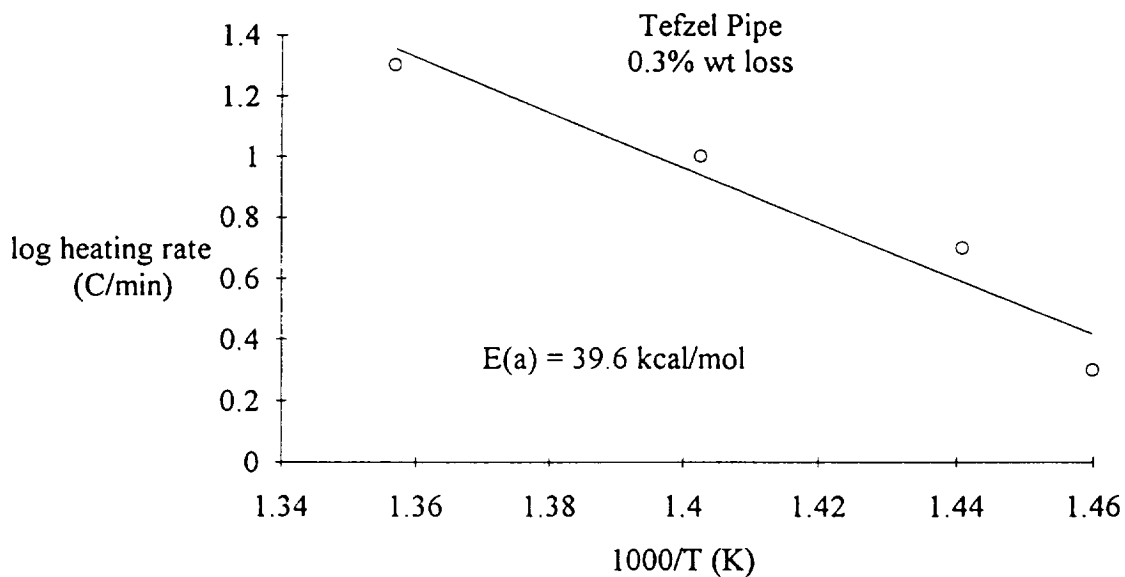


Figure 8 - Arrhenius plot obtained from varied heating rate experiments; temperature at 0.3% weight loss recorded; Tefzel pipe specimens.

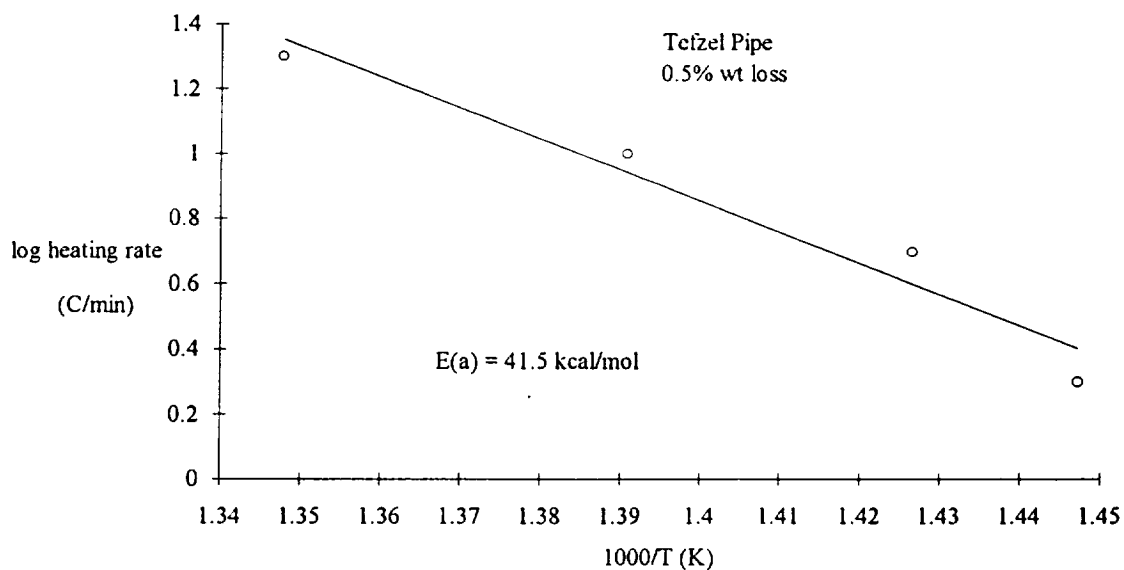


Figure 9 - Arrhenius plot obtained from varied heating rate experiments; temperature at 0.5% weight loss recorded; Tefzel pipe specimens.

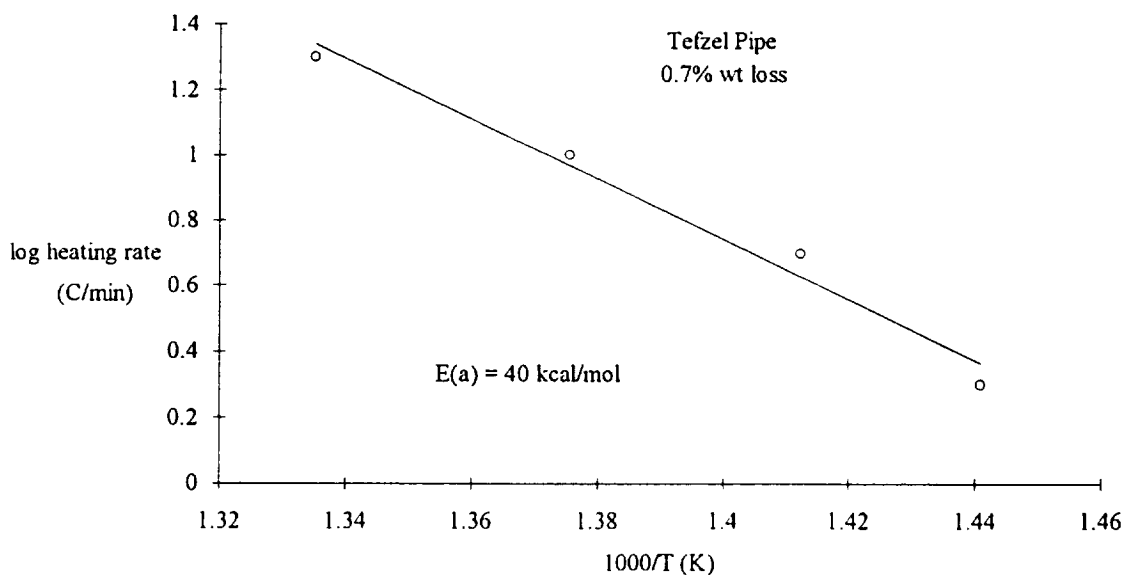


Figure 10 - Arrhenius plot obtained from varied heating rate experiments; temperature at 0.7% weight loss recorded; Tefzel pipe specimens.

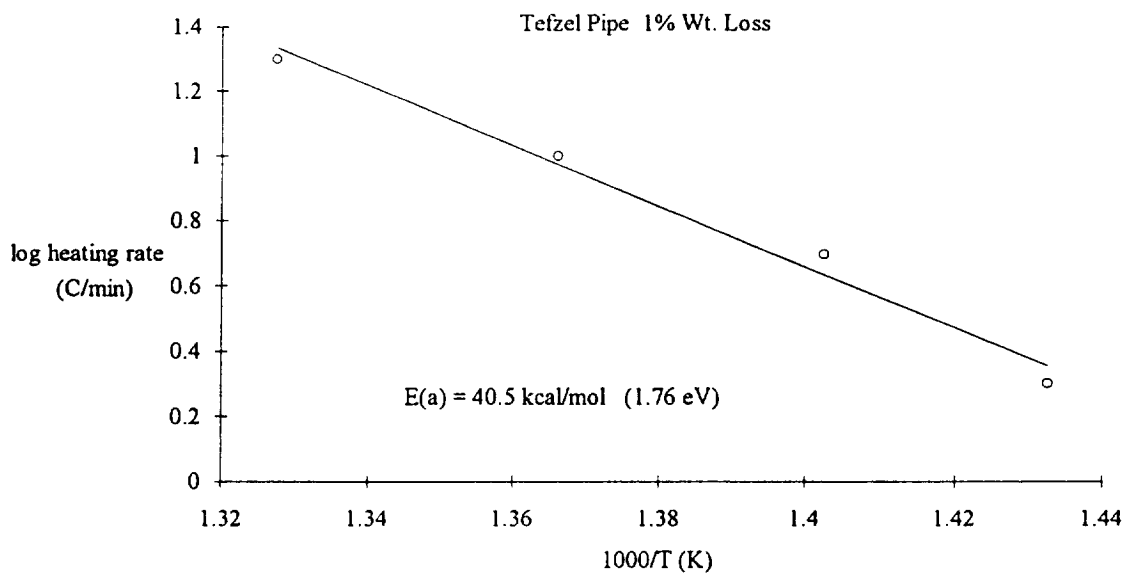


Figure 11 - Arrhenius plot obtained from varied heating rate experiments; temperature at 1% weight loss recorded; Tefzel pipe specimens.

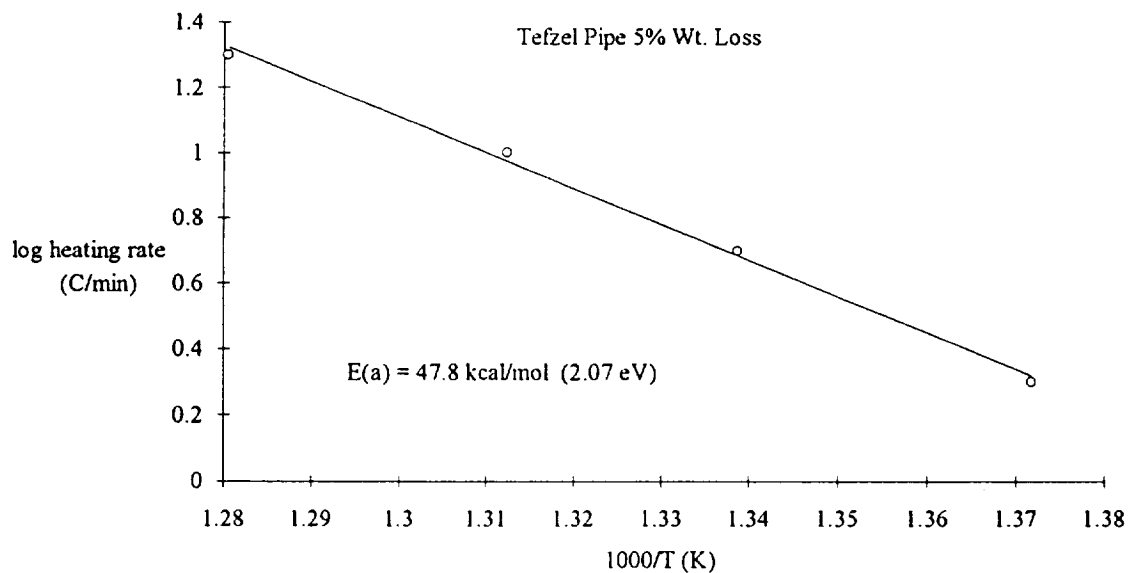


Figure 12 - Arrhenius plot obtained from varied heating rate experiments; temperature at 5% weight loss recorded; Tefzel pipe specimens.

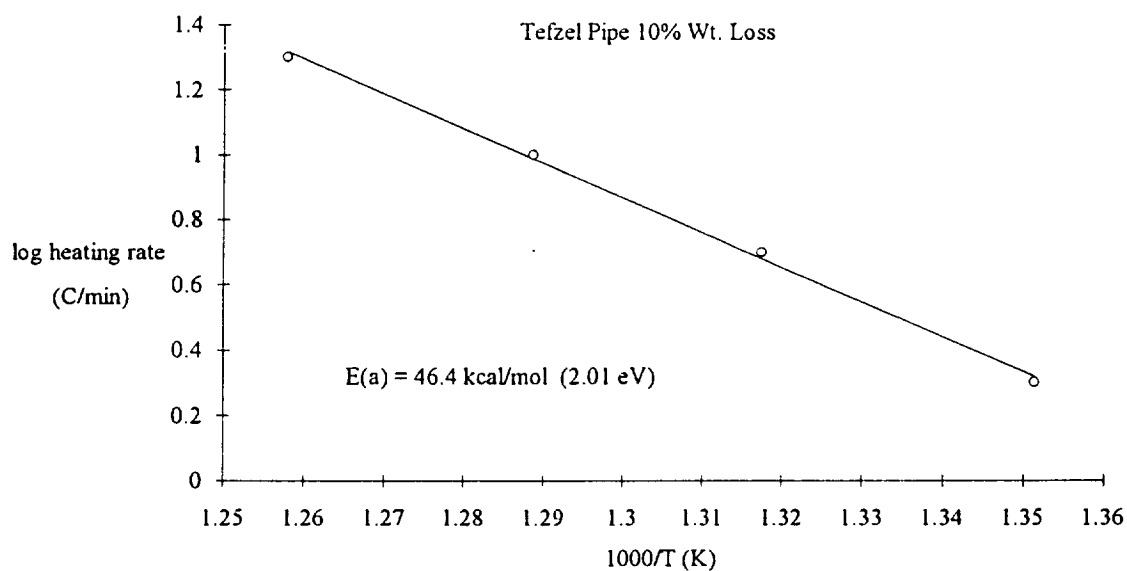


Figure 13 - Arrhenius plot obtained from varied heating rate experiments; temperature at 10% weight loss recorded; Tefzel pipe specimens.

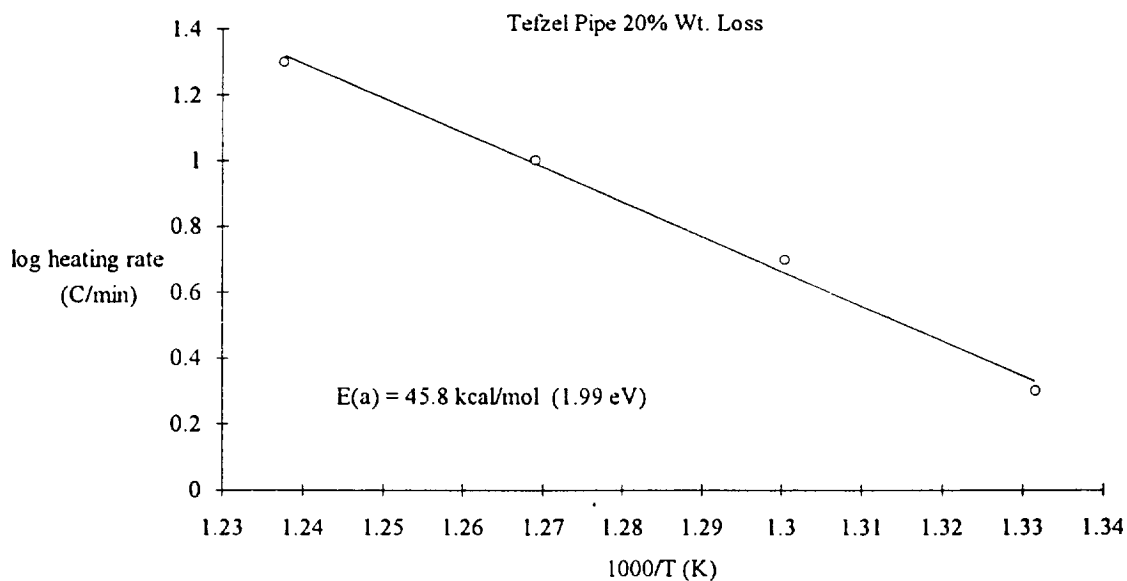


Figure 14 - Arrhenius plot obtained from varied heating rate experiments; temperature at 20% weight loss recorded; Tefzel pipe specimens.

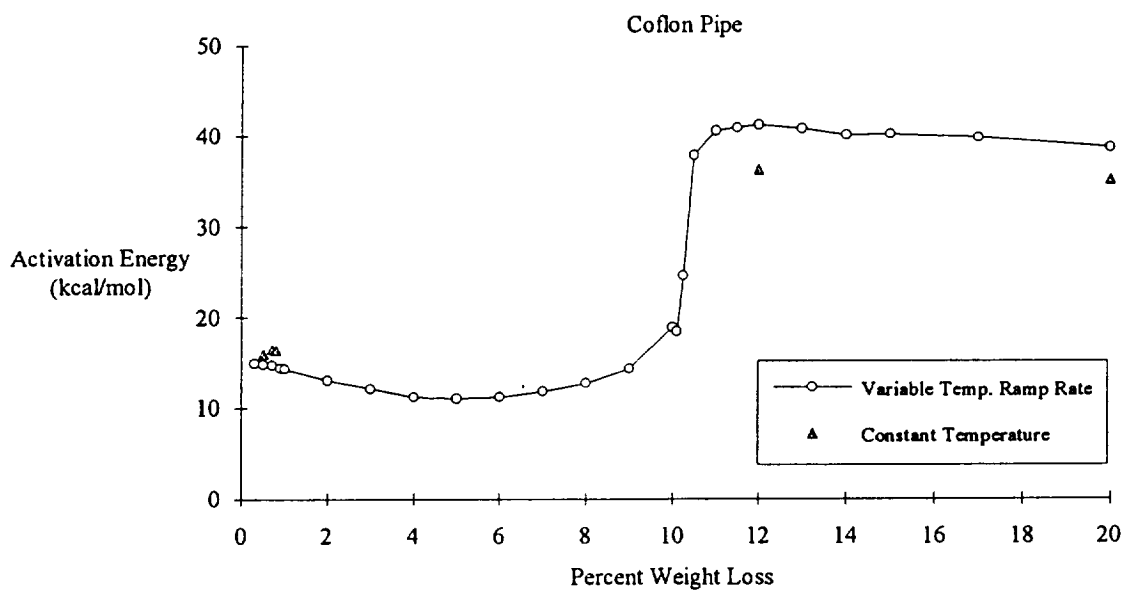


Figure 15 - Activation energy vs. percent weight loss; comparison of variable heating rate experiments and isothermal tests; Coflon Pipe.

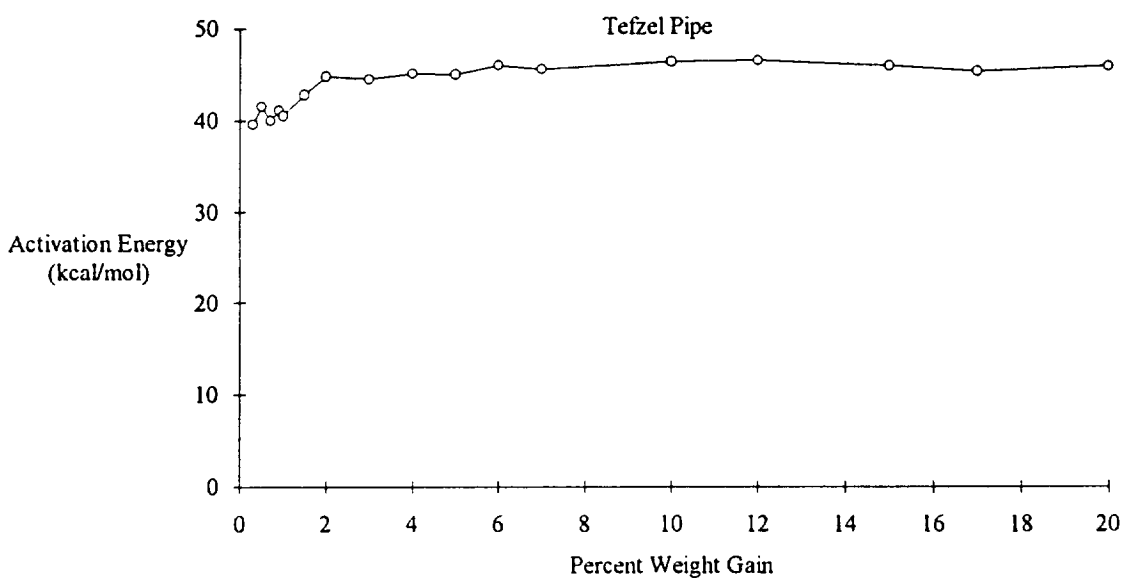


Figure 16 - Activation energy vs. percent weight loss; activation energies were obtained from variable heating rate experiments; Tefzel Ppe.

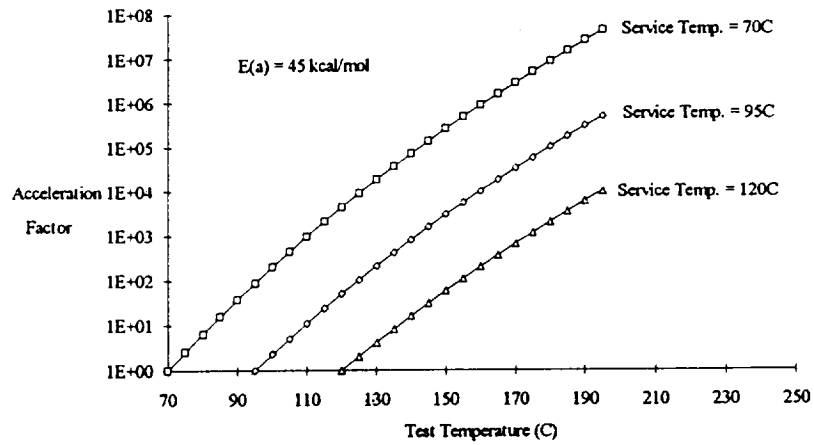


Figure 17 - Acceleration factors vs. test temperature at three service temperatures; activation energy = 45 kcal/mol.

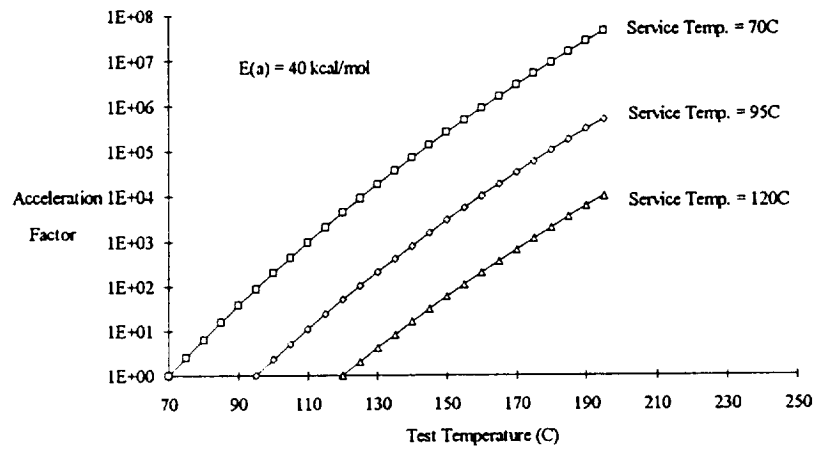


Figure 18 - Acceleration factors vs. test temperature at three service temperatures; activation energy = 40 kcal/mol.

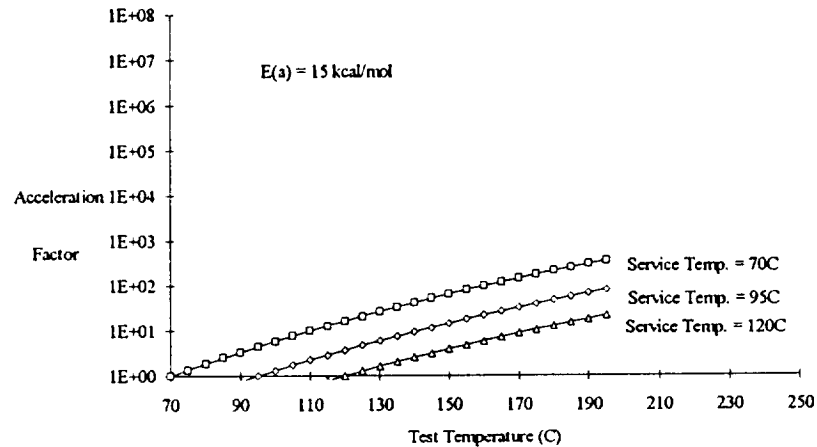


Figure 19 - Acceleration factors vs. test temperature at three service temperatures; activation energy = 15 kcal/mol.

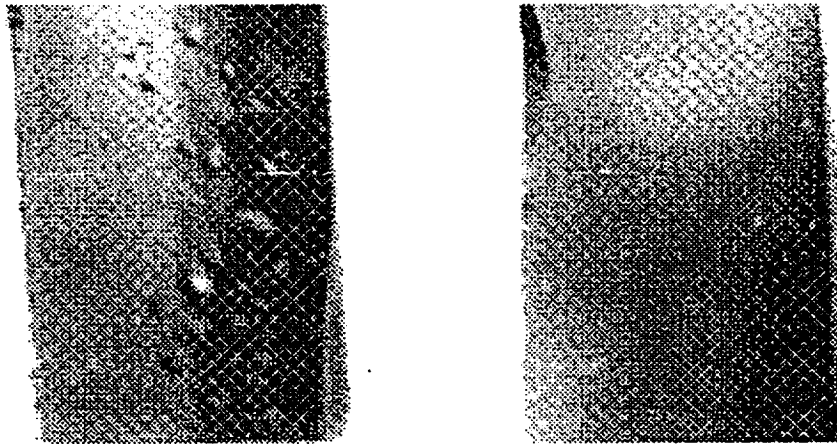


Figure 20 - Coflon before (rt) and after (lt) aging in 100°C oven for 24 hrs; inside diameter of the specimens shown. Specimen width = 10 mm.

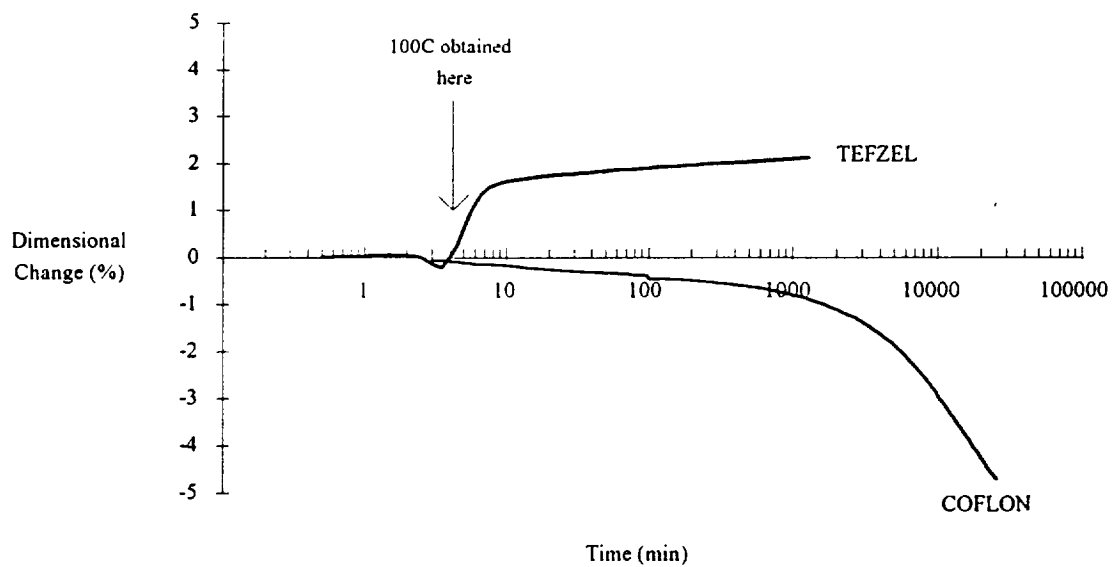


Figure - 21 Tefzel pipe-wall dimensional equilibrium at 100°C; Tefzel pipe specimen unaged, 3 mm wall thickness.

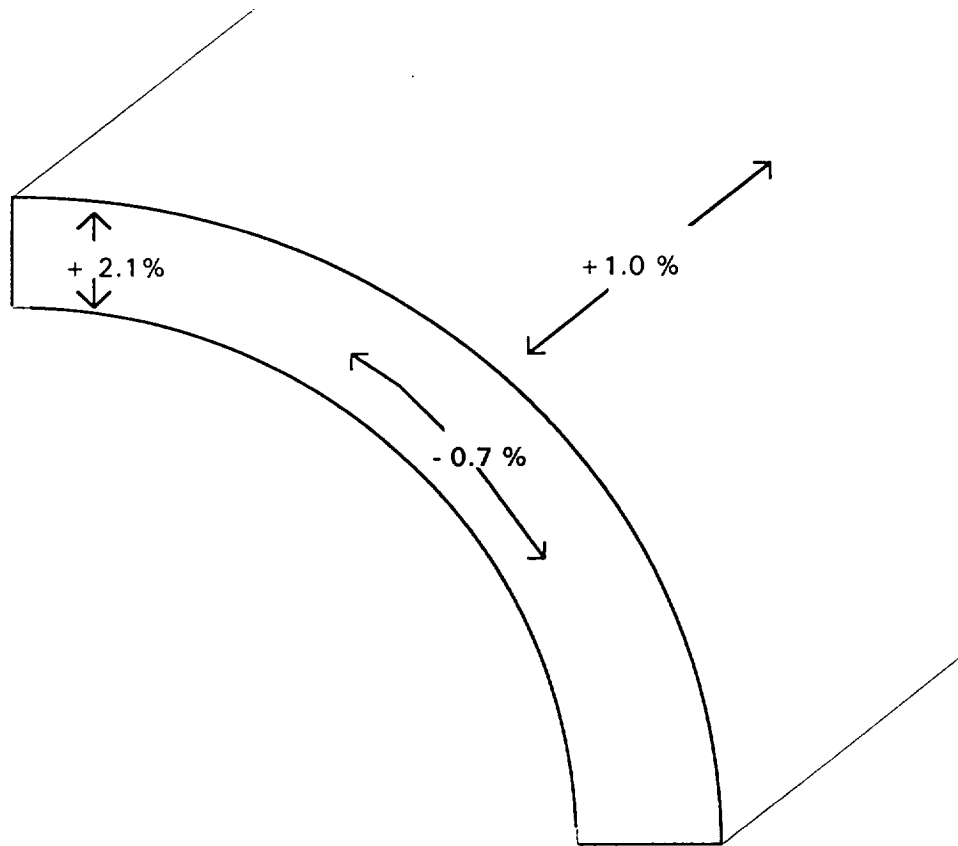


Figure 22 - Pipe wall dimensional change at 100°C isothermal for and Tefzel

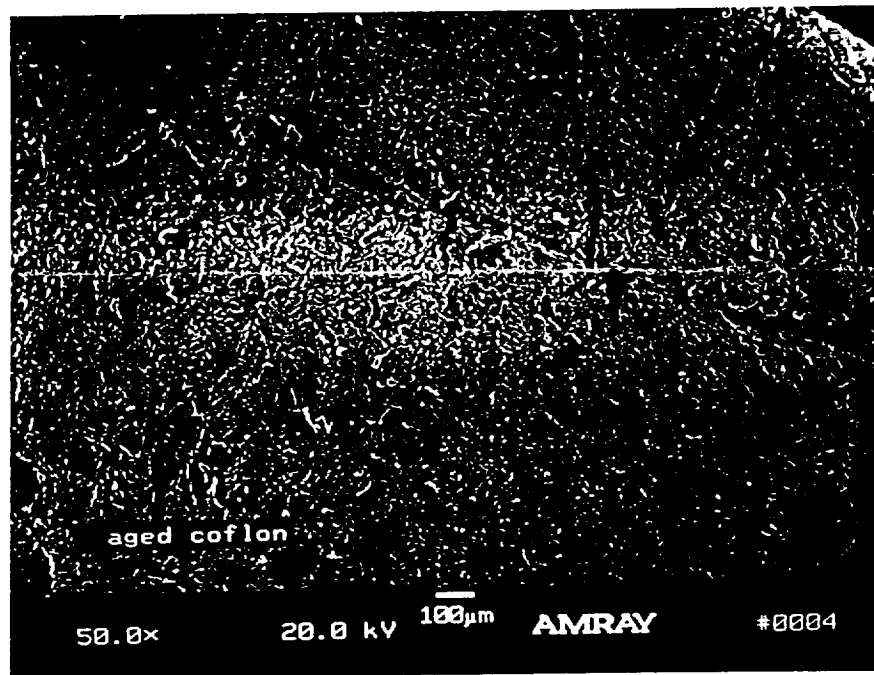


Figure 23 - Low Magnification (50x) SEM of Coflon Surface, Aged in 5% H₂S at 120°C for 7 days, Permeation performed in methane at 2500 psi and 130°C for 1 day.

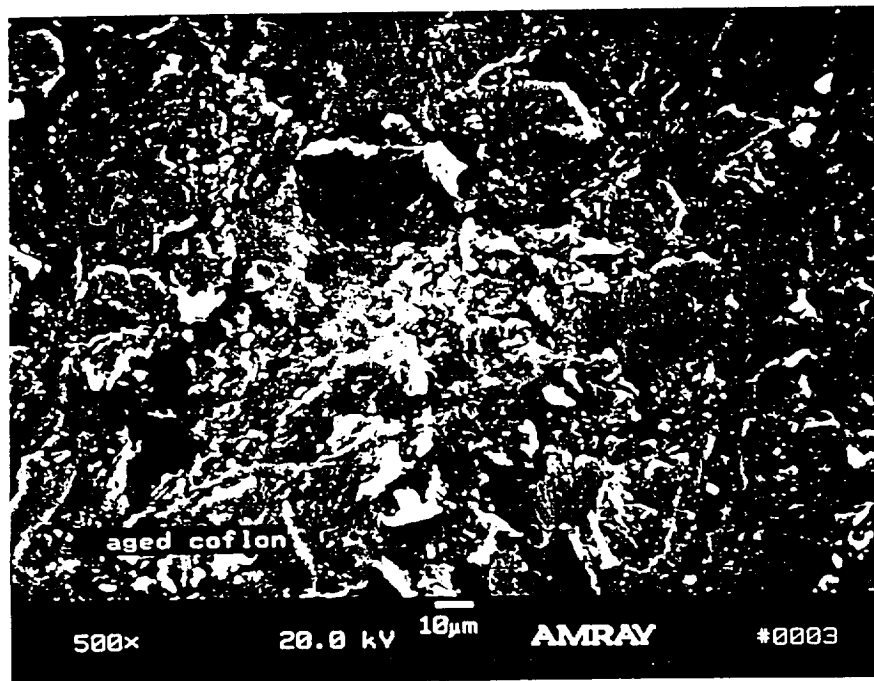


Figure 24 - SEM of Coflon Surface, 500x, Aged in 5% H₂S at 120°C for 7 days, Permeation performed in methane at 2500 psi and 130°C for 1 day.

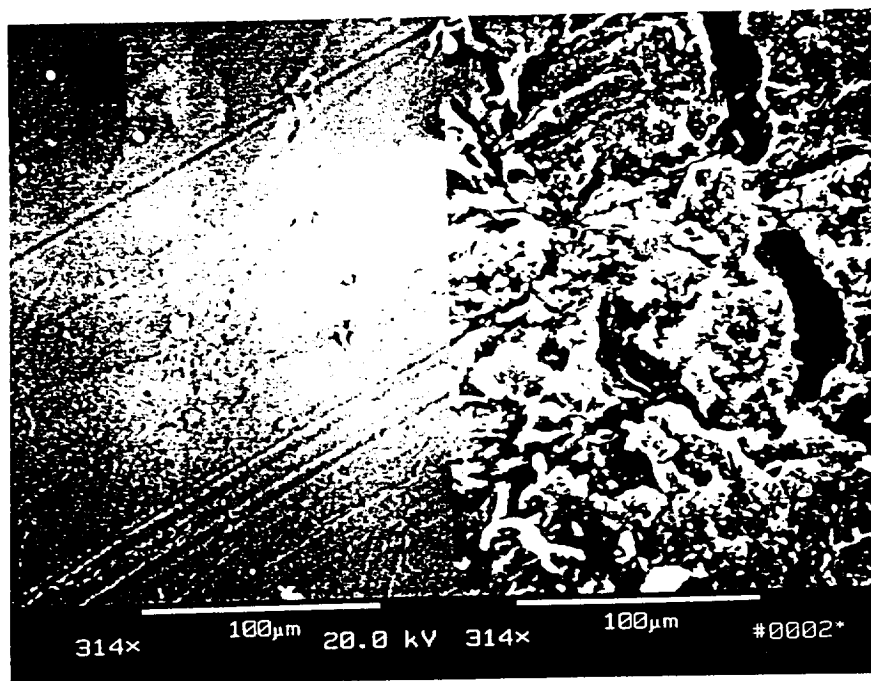


Figure 25 - Side-by-side SEM of Coflon Surface, 314x, Unaged vs Aged in 5% H₂S at 120°C for 7 days, Permeation performed in methane at 2500 psi and 130°C for 1 day.

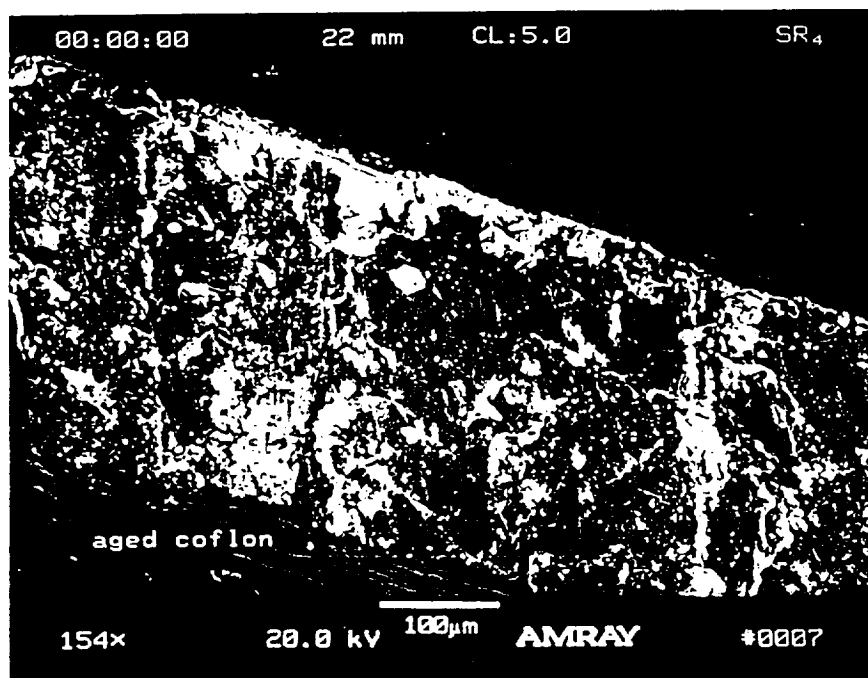


Figure 26 - SEM through the thickness of Coflon, 154x, Aged in 5% H₂S at 120°C for 7 days, Permeation performed in methane at 2500 psi and 130°C for 1 day.

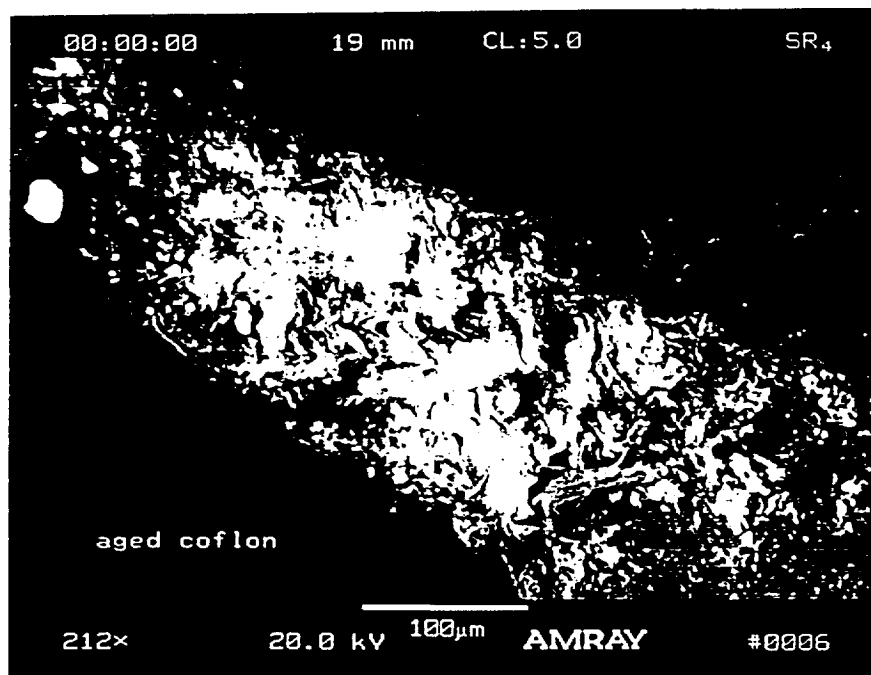


Figure 27 - SEM through the thickness of Coflon, 212x, Aged in 5% H₂S at 120°C for 7 days, Permeation performed in methane at 2500 psi and 130°C for 1 day.

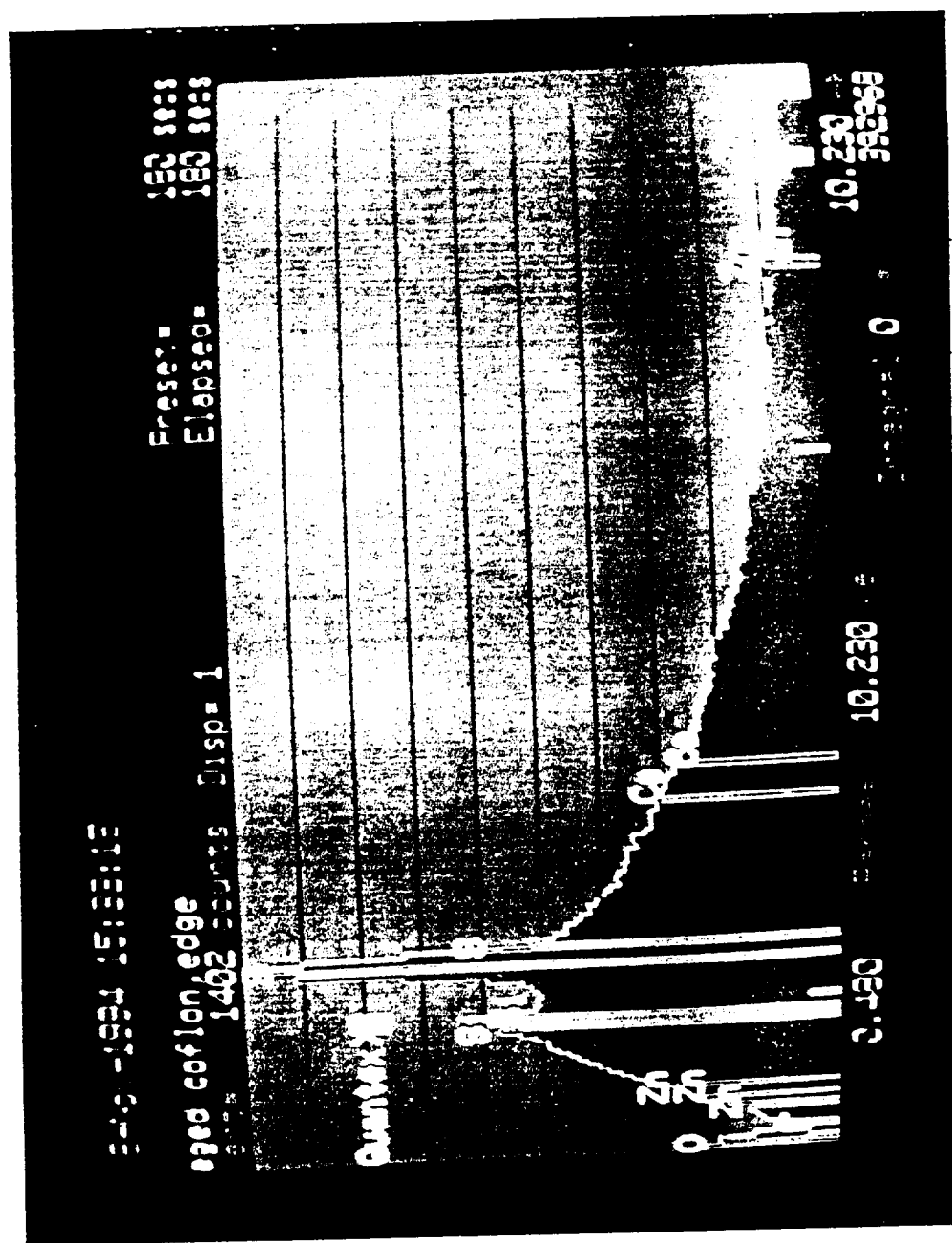


Figure 28 - X-RAY Spectra of Coflon specimen edge, Aged in 5% H₂S for 7 days, Permeation performed in methane at 2500 psi and 120°C.

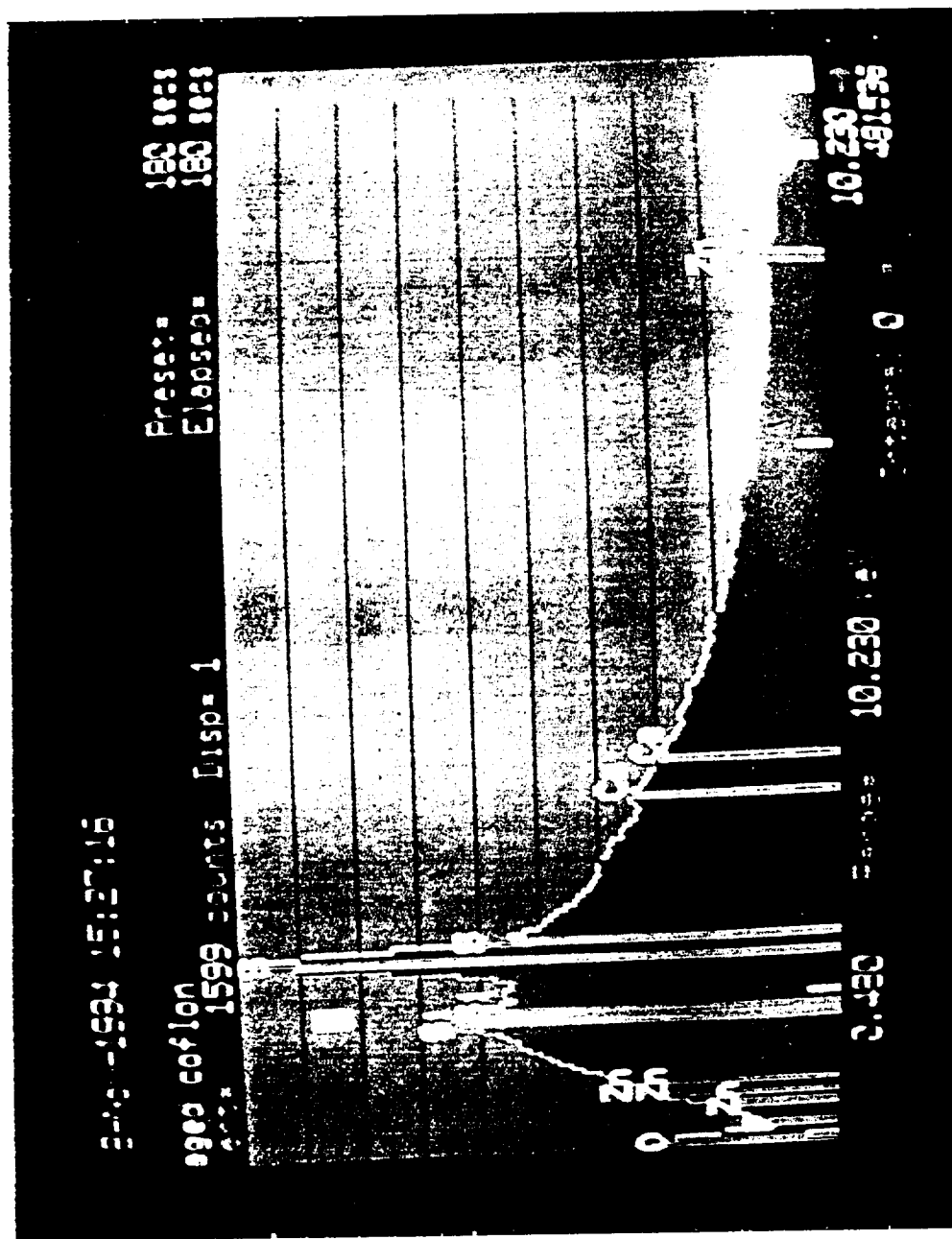


Figure 29 - X-RAY Spectra of Coflon specimen, Aged in 5% H₂S for 7 days, Permeation performed in methane at 2500 psi and 120°C.

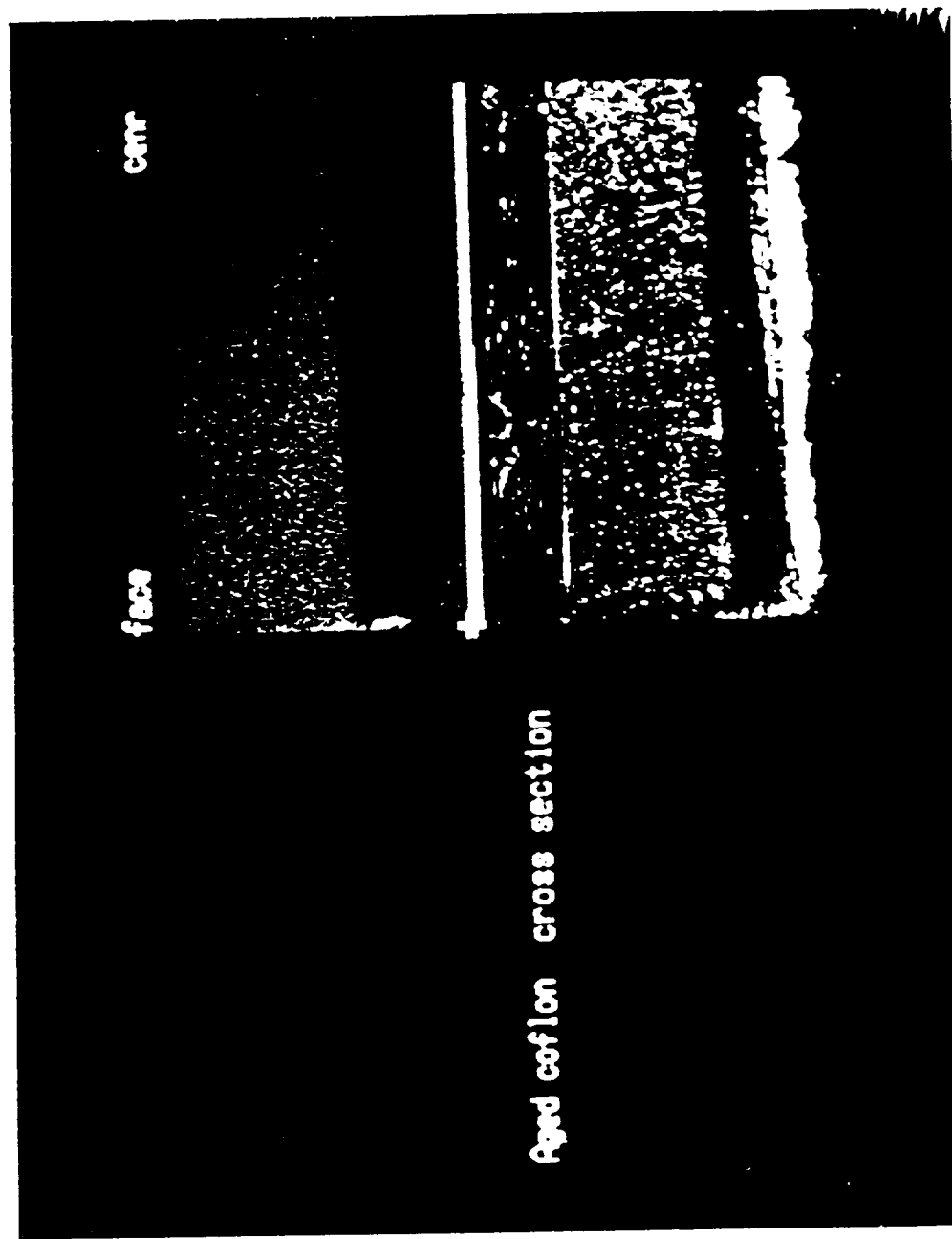


Figure 31 - X-Ray profile of Aged Coflon; upper left quadrant is Oxygen concentration profile; upper right quadrant is Sulfur concentration profile.